

PCT/RO-1390  
(REV. 5-93)U.S. DEPARTMENT OF COMMERCE  
PATENT AND TRADEMARK OFFICEATTORNEY'S DOCKET NUMBER  
10191/1714TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/786903

INTERNATIONAL APPLICATION NO.  
PCT/DE00/02124INTERNATIONAL FILING DATE  
29<sup>th</sup> June 2000  
(29.06.00)PRIORITY DATE CLAIMED:  
09 July 1999  
(09.07.99)

## TITLE OF INVENTION

SENSOR FOR DETERMINING A CONCENTRATION OF GAS COMPONENTS IN GAS MIXTURES

## APPLICANT(S) FOR DO/EO/US

Jens Stefan SCHNEIDER, Gerhard HOETZEL, Bernd SCHUMANN and Thomas MOSER


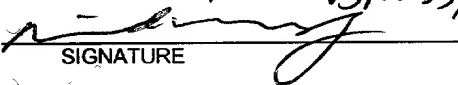
Applicant(s) herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) *immediately* rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) **UNSIGNED**.
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.  
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: International Search Report, and PCT/RO/101.

Express Mail No.: EL594611237US

APPLICATION NO. if known, see 37 C.F.R. 1.5 <b>09/786903</b>		INTERNATIONAL APPLICATION NO. PCT/DE00/02124		ATTORNEY'S DOCKET NUMBER 10191/1714	
17. <input checked="" type="checkbox"/> The following fees are submitted:  <b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b> Search Report has been prepared by the EPO or JPO ..... \$860.00  International preliminary examination fee paid to USPTO (37 CFR 1.482) .... \$690.00  No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... \$710.00  Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$1,000.00  International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... \$100.00				CALCULATIONS   PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$ 860	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	9 - 20 =	0	X \$18.00	\$0	
Independent Claims	1 - 3 =	0	X \$80.00	\$0	
Multiple dependent claim(s) (if applicable)			+ \$270.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$860	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$860	
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				+	\$
TOTAL NATIONAL FEE =				\$860	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				+	\$
TOTAL FEES ENCLOSED =				\$860	
				Amount to be:	
				refunded	\$
				charged	\$
a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed.					
b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>11-0600</u> in the amount of \$860.00 to cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>11-0600</u> . A duplicate copy of this sheet is enclosed.					
<b>NOTE:</b> Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
Kenyon & Kenyon		SIGNATURE			
One Broadway					
New York, New York 10004		Richard L. Mayer, Reg. No. 22,490			
26646		NAME			
PATENT TRADEMARK OFFICE		DATE <u>3/9/01</u>			

09/786903

JCO8 Rec'd PCT/PTO 09 MAR 2001

[10191/1714]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s) : SCHNEIDER et al.  
Serial No. : To Be Assigned  
Filed : Herewith  
For : SENSOR FOR DETERMINING A CONCENTRATION OF  
GAS COMPONENTS IN GAS MIXTURES  
Examiner : To Be Assigned  
Art Unit : To Be Assigned

Assistant Commissioner for Patents  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT AND  
37 C.F.R. § 1.125 SUBSTITUTE SPECIFICATION STATEMENT**

SIR:

Please amend the above-identified application before examination, as set forth below.

**IN THE SPECIFICATION AND ABSTRACT:**

In accordance with 37 C.F.R. § 1.121(b)(3), a Substitute Specification (including the Abstract but without claims) accompanies this response. It is respectfully requested that the Substitute Specification (and Abstract) be entered to replace the Specification of record.

**IN THE CLAIMS:**

On page 12, delete the first line, and insert:

-- What Is Claimed Is: --.

Please cancel claims 1-9, without prejudice.

Please add the following new claims:

10. (New) A sensor for determining a concentration of gas components in a gas mixture, comprising:

a first measuring electrode having substantially no catalytic effect on

EL594611237US

an establishment of an equilibrium in the gas mixture when exposed to the gas mixture, the first measuring electrode being a cermet electrode having at least one metal oxide component, the at least one metal oxide component being capable of reversible incorporation of oxygen;

a second measuring electrode catalyzing an establishment of an equilibrium in the gas mixture when exposed to the gas mixture; and

a solid electrolyte that is conductive for oxygen ions situated between the first and second measuring electrodes.

11. (New) The sensor according to claim 10, wherein the first measuring electrode is substantially composed of mixed oxides with a composition of one of  $\text{TiNiNbO}_x$  and  $\text{FeNiMnO}_4$ .

12. (New) The sensor according to claim 10, wherein the metal oxide component is at least one of  $\text{CeO}_2$  and  $\text{Mn}_2\text{O}_3$ .

13. (New) The sensor according to claim 10, wherein the first measuring electrode is a mixed potential electrode including at least one of gold and silver.

14. (New) The sensor according to claim 10, further comprising a porous layer, the solid electrolyte being integrated into the layer.

15. (New) The sensor according to claim 14, wherein the layer contains at least one of promoters and catalysts at least in some areas.

16. (New) The sensor according to claim 10, further comprising:

a reference electrode exposed to a reference gas; and

at least one layer composed of an oxygen conducting solid electrolyte situated between the reference electrode and the measuring electrodes.

17. (New) The sensor according to claim 10, further comprising a porous layer extending between the first and second measuring electrodes, one of the first and second measuring electrodes being situated on a side of the sensor facing the gas

mixture, another of the measuring electrodes being situated between a reference electrode and the one of the measuring electrodes facing the gas mixture.

18. (New) The sensor according to claim 17, wherein the one of the measuring electrodes facing the gas mixture is the first measuring electrode.

#### REMARKS

This Preliminary Amendment cancels, without prejudice, claims 1-9 in the underlying PCT Application No. PCT/DE00/02124, and adds new claims 10-18. The new claims conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

The amendments to the specification and abstract are to conform the specification and abstract to U.S. Patent and Trademark Office rules, and do not introduce new matter into the application.

The underlying PCT Application No. PCT/DE00/02124 includes an International Search Report, dated November 27, 2000, a copy of which is included. The Search Report includes a list of documents that were considered by the Examiner in the underlying PCT application.

Applicants assert that the present invention is new, non-obvious, and useful. Prompt consideration and allowance of the claims are respectfully requested.

Respectfully Submitted,

KENYON & KENYON

Dated: 3/9/01

By:

Richard L. Mayer  
Reg. No. 22,490

One Broadway  
New York, NY 10004  
(212) 425-7200

345122

1/PRTS

09/786903

JGOS Rec'd PCT/PTO 09 MAR 2001

[10191/1714]

SENSOR FOR DETERMINING A CONCENTRATION OF  
GAS COMPONENTS IN GAS MIXTURES

The present invention relates to a sensor for determining a concentration of gas components in gas mixtures having the features characterized in Claim 1.

5 Background Information

Sensors for determining the concentration of gas components in gas mixtures, in particular in gases from internal combustion engines, are known. Such sensors are used to preset a fuel/air mixture for operation of the internal combustion engine on the basis of a determination of the oxygen concentration and/or the concentration of reducing gas components such as HC or CO. A specific operating state can be characterized by using the ratio of the oxygen concentration to the fuel concentration. If there is a stoichiometric excess of fuel (rich range), the amount of oxygen in the exhaust gas will be small in comparison with other components, which are partially uncombusted. In the lean range, where oxygen from air is predominant in the fuel/air mixture, the oxygen concentration in the exhaust gas is accordingly high.

To determine the oxygen concentration in the exhaust gas, there are known lambda sensors which detect a lambda value  $> 1$  in a lean range, a lambda value  $< 1$  in the rich range and a lambda value  $= 1$  in a stoichiometric range. In a known manner, an electrochemical measuring cell of the sensor supplies a detection voltage which is sent to a circuit arrangement. The detection voltage depends on an oxygen concentration difference at the at least two measuring electrodes used. A solid electrolyte body which is conductive for oxygen ions is arranged between the measuring electrodes. The detection voltage increases or decreases according to the oxygen

EL594611237US

concentration in the exhaust gas.

In addition, there are known sensors which are used to determine the concentration of the reducing gas components.

5 These sensors are often component specific, i.e., there is a separate sensor for each gas component ( $H_2$ , HC and CO) to be detected.

10 Both types of sensor supply either a value for the oxygen concentration or the concentration of the reducing gas components. Thus, they supply values which give only an indirect indication of the status of the lambda value. Thus, a sensor for determining oxygen concentrations can supply a certain absolute oxygen concentration from which it is possible to infer the composition of the fuel/air mixture.

15 A more precise setting of a control status of an internal combustion engine can be achieved by determining the lambda value directly. It is advantageous here to have a compact sensor capable of handling both sensor functions instead of two separate sensors, one for each gas component. Previous attempts to accommodate multiple sensor functions on one substrate have resulted in a complicated layout or a complicated layer structure which has a greater susceptibility to faults and entails high manufacturing costs.

20 The reducing gas components in the exhaust gas of internal combustion engines are in a thermodynamic equilibrium with the oxygen. The further away the sensors are arranged from the engine in an exhaust duct of the internal combustion engine, the lower the temperature of the exhaust gas, and thus it is difficult to establish a thermodynamic equilibrium from a kinetic standpoint. It is known that the equilibrium reaction can be catalyzed with transition metals. In particular, catalysts containing platinum, palladium or rhodium have

proven suitable. In using these metals as the electrode material for the measuring electrodes of sensors, it has proven especially advantageous to have such a catalytic activity on a measuring electrode which is exposed to the exhaust gas. In this way, the oxygen concentration at this measuring electrode can be kept very low, thus yielding a very high potential difference with respect to another electrode exposed to a reference gas. However, such a measuring electrode which catalyzes the establishment of an equilibrium in the gas mixture (equilibrium electrode) does not permit detection of the concentration of the reducing gas components.

Therefore, it is known that materials which inhibit a catalytic effect of the measuring electrode can be added to the measuring electrode exposed to the gas mixture. Thus, German Patent 44 08 361 C2 describes a measuring electrode in which adsorption of oxygen on a surface of the measuring electrode has been made possible by the addition of bismuth, platinum, antimony or lead. Thus, the oxygen concentration, which determines the potential of the measuring electrode, at a ternary boundary of the measuring electrode is kept almost constant in operation of the internal combustion engine at  $\lambda > 1$ . The measuring electrode designed in this way reacts essentially to oxygen and is thus a non-equilibrium electrode or a mixed potential electrode. Such a measuring electrode can thus be used as a reference electrode at  $\lambda > 1$ .

In addition, it is known from German Patent 44 08 504 that such a mixed potential electrode can be designed by admixture of gold and/or silver. Due to the admixture of gold and/or silver, the catalytic conversion is inhibited by oxidation of CO and/or HC and reduction of  $\text{NO}_x$ . The high affinity of these metals for the reducing gas components is utilized at the measuring electrode. The oxygen concentration and thus the



potential of the mixed potential electrode can be kept almost constant due to adsorption of the reducing gas components at the surface of the mixed potential electrode in operation of the internal combustion engine at  $\lambda < 1$ . In this way, such a measuring electrode can be used as a reference electrode at  $\lambda < 1$ . One disadvantage of these two described embodiments of mixed potential electrodes is that they permit only constant potentials for two extreme positions of the  $\lambda$  value and thus omit the range at  $\lambda$  values  $\approx 1$ , which is especially interesting for control of the control status of the internal combustion engine. In addition, it is impossible in this way to determine the oxygen concentration on the one hand or the concentration of reducing gas components on the other hand by using one and the same measuring electrode.

#### Advantages of the Invention

It is possible to determine either the oxygen concentration or the concentration of a reducing gas component with an arrangement of just two measuring electrodes by means of the features of Claim 1 and by using the sensor according to the present invention for determining a concentration of gas components in gas mixtures having a first measuring electrode (mixed potential electrode) which has little or no catalytic effect on the establishment of an equilibrium in the gas mixture and a second measuring electrode (equilibrium electrode) which catalyzes the establishment of an equilibrium in the gas mixture as well as a solid electrolyte that is conductive for oxygen ions arranged between the two measuring electrodes, with the two measuring electrodes being exposed to the gas mixture. Due to the fact that at least the first measuring electrode is a cermet electrode, where at least one metal oxide component of the cermet electrode is capable of reversible incorporation of oxygen, the potential of this

first measuring electrode is kept almost constant in the range around  $\lambda \approx 1$ . Thus, the first measuring electrode is the reference electrode in this operating state of the internal combustion engine, while the second measuring electrode functions as the working electrode. If the operating state of the internal combustion engine changes to a range with  $\lambda > 1$ , then the potential of the second measuring electrode is almost constant, while the potential of the first measuring electrode is variable and is determined essentially by the concentration of the reducing gas components. Thus in this case the second measuring electrode is the reference electrode and the first measuring electrode is the working electrode.

Suitable metal oxide components for the first measuring electrode include, for example, the mixed oxides such as  $\text{TiNiNbO}_x$  or  $\text{FeNiMnO}_4$ . Furthermore, a noble metal such as gold may also be incorporated into the first measuring electrode. It is thus possible to adapt the potential of the first measuring electrode very accurately to the requirements of a given application.

In a preferred embodiment of the present invention, a reference electrode additionally exposed to a reference gas is provided for the two measuring electrodes exposed to the gas mixture. The measuring electrodes may be arranged side by side, i.e., both in the same layer of a multilayer sensor. However, it is also conceivable for the two measuring electrodes to be arranged one after the other in different layers, starting from an outer side of the sensor in the direction of the reference electrode. One layer between the two measuring electrodes must be sufficiently porous so that it allows a sufficiently rapid establishment of an equilibrium in the constantly changing concentrations of the individual exhaust gas components. One measuring electrode corresponds to the mixed potential electrode based on oxygen-storing metal

oxide components and the other measuring electrode is designed as an equilibrium electrode.

5 It has proven advantageous to arrange the mixed potential electrode closer to the exhaust gas because it has an especially stable and constant potential in rapid gas changes at lambda values around 1. In addition to an equilibrium electrode which naturally has a catalytic activity, it is also conceivable to incorporate additional catalysts or promoters  
10 into the porous intermediate layer, although of course not in the immediate vicinity of the mixed potential electrode. In this way, it is possible to have a controlled influence on the establishment of an equilibrium in the mixture, thus yielding the possibility of using other metal components that are not  
15 catalytically active for the equilibrium electrode.

With the help of this preferred arrangement with a total of only three electrodes, the oxygen concentration and the concentration of the reducing gas components can be determined  
20 simultaneously in certain operating states and thus the status of the lambda value can be determined directly. This permits a much more rapid and accurate establishment of the control status of the internal combustion engine. In addition, such a sensor can be implemented in an especially simple and  
25 inexpensive manner.

Other preferred embodiments of the present invention are derived from the other features characterized in the subordinate claims.

30 Drawing

The present invention is illustrated in greater detail below in embodiments on the basis of the respective drawings.

Figure 1 shows a schematic sectional view through a sensor,  
and

Figure 2 shows a schematic sectional view through another  
embodiment of a sensor.

5

#### Description of Embodiments

Figure 1 shows a sensor 10 which can be used for determination  
of the concentration of gas components in gas mixtures, in  
particular the exhaust gases of internal combustion engines.  
Such a sensor 10 is preferably composed of individual ceramic  
layers which may be structured in a known way by screen  
printing, lamination, cutting, sintering or the like. Sensor  
10 contains an electrochemical measuring cell 12 having a  
first measuring electrode 14 and a second measuring electrode  
16, with a porous oxygen ion conducting layer 18 extending  
between two measuring electrodes 14, 16. A heating element 22  
is arranged beneath second measuring electrode 16 in a layer  
20 which at least conducts heat well. Heating element 22  
includes a resistance element 24, designed as a meandering  
element here, and it functions to establish or control an  
operating temperature of sensor 10. Second measuring electrode  
16 is composed of a noble metal cermet, e.g., based on a noble  
metal such as platinum. This second measuring electrode 16 is  
referred to below as equilibrium electrode 16 because of the  
catalytic activity of these noble metals with regard to the  
equilibrium reaction between oxygen and reducing gas  
components of the exhaust gas as explained below. As also to  
be explained below, first measuring electrode 14 has little or  
no catalytic activity in certain operating states of the  
internal combustion engine, which can be characterized by a  
lambda value, and it is referred to below as mixed potential  
electrode 14.

During combustion of a fuel/air mixture in the internal

combustion engine, reducing gas components which can react with the oxygen and are thus in a thermodynamic equilibrium with it are formed in variable amounts. In addition to a temperature-dependent equilibrium status of this reaction, the kinetics of the reaction is especially important for establishing the equilibrium. It may essentially be assumed that the temperature of the exhaust gas drops with an increase in the distance of sensor 10 from the engine, and thus it becomes more difficult for a thermodynamic equilibrium to be established from a kinetic standpoint. Due to the noble metals such as platinum, palladium and rhodium used in equilibrium electrode 16, establishment of this equilibrium is catalyzed. Thus, the potential of equilibrium electrode 16 is determined essentially by the oxygen concentration.

The potential of mixed potential electrode 14, however, does not depend on the oxygen concentration, at least in some ranges, but instead it is a function of the concentration of reducing gas components. It is thus possible to influence the potential of mixed potential electrode 14 in a controlled manner by selecting at least one metal oxide component capable of reversible incorporation of oxygen. Such a mixed potential electrode 14 may be made mostly of  $\text{TiNiNbO}_x$  or  $\text{FeNiMnO}_4$ . It is also conceivable to use metal oxides such as  $\text{Mn}_2\text{O}_3$  and  $\text{CeO}_2$ . In addition, the cermet electrode may also contain as an added metal component a noble metal such as gold or silver. In this way, the potential of mixed potential electrode 14 can be adapted individually to the requirements of given applications.

In an operating mode of internal combustion engine where  $\lambda \approx 1$ , the oxygen concentration directly at a surface of mixed potential electrode 14 is kept almost constant due to the added metal oxide components. A capacity for incorporation and disincorporation of oxygen in a mixed potential electrode 14

determines a lambda range in which the potential of mixed potential electrode 14 is almost constant. However, the potential on equilibrium electrode 16 in such an operating mode of the internal combustion engine is exposed to great variations, because there are great variations in oxygen concentration precisely in such a lambda range. Thus at  $\lambda \approx 1$ , mixed potential electrode 14 can be used as a reference electrode, while equilibrium electrode 16 can be used as a working electrode 16. Then a detection voltage U which is a direct measure of the oxygen concentration of the gas mixture can be picked off via electrochemical measuring cell 12.

When the operating mode of the internal combustion engine changes to a range of  $\lambda > 1$ , then the potential of mixed potential electrode 14 changes greatly with a change in the concentration of the reducing gas components. However, the potential of equilibrium electrode 16 is almost constant at high oxygen concentrations. Thus in this case, equilibrium electrode 16 functions as the reference electrode and mixed potential electrode 14 functions as the working electrode. Then a detection voltage U corresponding to the concentration of the reducing gas components can be picked off via electrochemical measuring cell 12.

In principle, an arrangement of two measuring electrodes 14, 16 may be in the opposite order from that shown here, but in the case of the arrangement shown here, additional promoters or catalysts that support the establishment of an equilibrium may be incorporated into layer 18. In this way it is possible to vary the composition of equilibrium electrode 16 to a great extent, and it is not necessary to use such relatively expensive noble metals as platinum or palladium.

Figure 2 shows a preferred additional embodiment of sensor 10. In addition to two measuring electrodes 14, 16 described

above, sensor 10 has another reference electrode 26. Reference electrode 26 is above a reference channel 28 which is filled with a reference gas. Heating device 22 is used first for heating sensor 10 and also for heating the reference gas.

5 Between reference electrode 26 and equilibrium electrode 16 there is a layer 30 composed of a solid electrolyte that is conductive for oxygen ions.

10 Such a sensor 10 has a first electrochemical measuring cell 32, which includes mixed potential electrode 14 and reference electrode 26, and a second electrochemical measuring cell 34, which includes equilibrium electrode 16 and reference electrode 26.

15 With the help of this very simple arrangement with only three electrodes, the oxygen concentration and the concentration of the reducing gas components can be measured simultaneously as a function of the operating mode of the internal combustion engine. In this way, a lambda value can be determined very  
20 rapidly and with high precision.

Thus, for example, at a lambda value  $> 1$ , the potential of mixed potential electrode 14 depends essentially on the concentration of the reducing gas components, as mentioned  
25 above, and thus it can be picked off as a detection voltage  $U_1$  via electrochemical measuring cell 32. In the same operating mode, a potential difference between equilibrium electrode 16 and reference electrode 26 can also be detected if the reference gas has a sufficiently different oxygen  
30 concentration. The potential difference then leads to a detection voltage  $U_2$  which can be picked off at electrochemical measuring cell 34 and is a direct measure of the oxygen concentration.

35 In addition to the arrangement shown here, where measuring

electrodes 14, 16 are arranged in successive layers of sensor 10, an arrangement in one and the same layer is also conceivable. In this way, sensor 10 is also simpler to manufacture, i.e., fewer steps are involved.



## Patent Claims

1. A sensor for determining a concentration of gas components in gas mixtures having a first measuring electrode (mixed potential electrode) which has little or no catalytic effect on the establishment of an equilibrium in the gas mixture and a second measuring electrode (equilibrium electrode) which catalyzes the establishment of an equilibrium in the gas mixture as well as a solid electrolyte that is conductive for oxygen ions arranged between the two measuring electrodes, with the two measuring electrodes being exposed to the gas mixture,

characterized in that at least the first measuring electrode (14) is a cermet electrode, where at least one metal oxide component of the cermet electrode is capable of reversible incorporation of oxygen.

2. The sensor according to Claim 1, characterized in that the mixed potential electrode (14) is made largely of mixed oxides with the composition  $\text{TiNiNbO}_x$  or  $\text{FeNiMnO}_4$ .

3. The sensor according to Claim 1, characterized in that the metal oxide component is  $\text{CeO}_2$  and/or  $\text{Mn}_2\text{O}_3$ .

4. The sensor according to one of Claims 1 through 3, characterized in that gold and/or silver is added to the mixed potential electrode (14).

5. The sensor according to one of Claims 1 through 4, characterized in that the solid electrolyte that is conductive for oxygen ions is integrated into a layer (18) of the sensor (10), and this layer (18) is porous.

6. The sensor according to Claim 5, characterized in that the layer (18) contains promoters and/or catalysts at least in some areas.

7. The sensor according to one of Claims 1 through 6, characterized in that a reference electrode (26) which is exposed to a reference gas is provided for the sensor (10), and at least one layer (18, 30) made of an oxygen conducting solid electrolyte is provided between the reference electrode (26) and the measuring electrodes (14, 16).

8. The sensor according to Claim 7, characterized in that one of the measuring electrodes (14, 16) is arranged on a side of the sensor (10) facing the gas mixture, and the other measuring electrode (14, 16) is between the reference electrode (26) and the measuring electrode (14, 16) facing the gas mixture, with the porous layer (18) extending between the two measuring electrodes (14, 16).

9. The sensor according to Claim 8, characterized in that the measuring electrode (14, 16) facing the gas mixture is the mixed potential electrode (14).

## Abstract

A sensor is described for determining a concentration of gas components in gas mixtures having a first measuring electrode (mixed potential electrode) which has little or no catalytic effect on the establishment of an equilibrium in the gas mixture and a second measuring electrode (equilibrium electrode) which catalyzes the establishment of an equilibrium in the gas mixture as well as a solid electrolyte that is conductive for oxygen ions arranged between the two measuring electrodes, with the two measuring electrodes being exposed to the gas mixture.

At least the first measuring electrode (16) is a cermet electrode, where at least one metal oxide component of the cermet electrode is capable of reversible incorporation of oxygen.

(Figure 1)

345096

SENSOR FOR DETERMINING A CONCENTRATION OF  
GAS COMPONENTS IN GAS MIXTURES

Background Information

Sensors for determining the concentration of gas components in gas mixtures, in particular in gases from internal combustion engines, are known. Such sensors are used to preset a fuel/air mixture for operation of the internal combustion engine on the basis of a determination of the oxygen concentration and/or the concentration of reducing gas components such as HC or CO. A specific operating state can be characterized by using the ratio of the oxygen concentration to the fuel concentration. If there is a stoichiometric excess of fuel (rich range), the amount of oxygen in the exhaust gas will be small in comparison with other components, which are partially uncombusted. In the lean range, where oxygen from air is predominant in the fuel/air mixture, the oxygen concentration in the exhaust gas is accordingly high.

To determine the oxygen concentration in the exhaust gas, there are known lambda sensors which detect a lambda value  $> 1$  in a lean range, a lambda value  $< 1$  in the rich range and a lambda value  $= 1$  in a stoichiometric range. In a known manner, an electrochemical measuring cell of the sensor supplies a detection voltage which is sent to a circuit arrangement. The detection voltage depends on an oxygen concentration difference at the at least two measuring electrodes used. A solid electrolyte body which is conductive for oxygen ions is arranged between the measuring electrodes. The detection voltage increases or decreases according to the oxygen concentration in the exhaust gas.

In addition, there are known sensors which are used to determine the concentration of the reducing gas components.

SUBSTITUTE SPECIFICATION

EL594611237US

These sensors are often component specific, i.e., there is a separate sensor for each gas component ( $H_2$ , HC and CO) to be detected.

5 Both types of sensor supply either a value for the oxygen concentration or the concentration of the reducing gas components. Thus, they supply values which give only an indirect indication of the status of the lambda value. Thus, a sensor for determining oxygen concentrations can supply a  
10 certain absolute oxygen concentration from which it is possible to infer the composition of the fuel/air mixture.

15 A more precise setting of a control status of an internal combustion engine can be achieved by determining the lambda value directly. It is advantageous here to have a compact sensor capable of handling both sensor functions instead of two separate sensors, one for each gas component. Previous attempts to accommodate multiple sensor functions on one substrate have resulted in a complicated layout or a  
20 complicated layer structure which has a greater susceptibility to faults and entails high manufacturing costs.

25 The reducing gas components in the exhaust gas of internal combustion engines are in a thermodynamic equilibrium with the oxygen. The further away the sensors are arranged from the engine in an exhaust duct of the internal combustion engine, the lower the temperature of the exhaust gas, and thus it is difficult to establish a thermodynamic equilibrium from a kinetic standpoint. It is known that the equilibrium reaction  
30 can be catalyzed with transition metals. In particular, catalysts containing platinum, palladium or rhodium have proven suitable. In using these metals as the electrode material for the measuring electrodes of sensors, it has proven especially advantageous to have such a catalytic  
35 activity on a measuring electrode which is exposed to the

exhaust gas. In this way, the oxygen concentration at this measuring electrode can be kept very low, thus yielding a very high potential difference with respect to another electrode exposed to a reference gas. However, such a measuring electrode which catalyzes the establishment of an equilibrium in the gas mixture (equilibrium electrode) does not permit detection of the concentration of the reducing gas components.

Therefore, it is known that materials which inhibit a catalytic effect of the measuring electrode can be added to the measuring electrode exposed to the gas mixture. Thus, German Patent No. 44 08 361 describes a measuring electrode in which adsorption of oxygen on a surface of the measuring electrode has been made possible by the addition of bismuth, platinum, antimony or lead. Thus, the oxygen concentration, which determines the potential of the measuring electrode, at a ternary boundary of the measuring electrode is kept almost constant in operation of the internal combustion engine at  $\lambda > 1$ . The measuring electrode designed in this way reacts essentially to oxygen and is thus a non-equilibrium electrode or a mixed potential electrode. Such a measuring electrode can thus be used as a reference electrode at  $\lambda > 1$ .

In addition, it is known from German Patent No. 44 08 504 that such a mixed potential electrode can be designed by admixture of gold and/or silver. Due to the admixture of gold and/or silver, the catalytic conversion is inhibited by oxidation of CO and/or HC and reduction of  $\text{NO}_x$ . The high affinity of these metals for the reducing gas components is utilized at the measuring electrode. The oxygen concentration and thus the potential of the mixed potential electrode can be kept almost constant due to adsorption of the reducing gas components at the surface of the mixed potential electrode in operation of the internal combustion engine at  $\lambda < 1$ . In this way,

such a measuring electrode can be used as a reference electrode at  $\lambda < 1$ . One disadvantage of these two described embodiments of mixed potential electrodes is that they permit only constant potentials for two extreme positions of the  $\lambda$  value and thus omit the range at  $\lambda$  values  $\approx 1$ , which is especially interesting for control of the control status of the internal combustion engine. In addition, it is impossible in this way to determine the oxygen concentration on the one hand or the concentration of reducing gas components on the other hand by using one and the same measuring electrode.

#### Summary Of The Invention

It is possible to determine either the oxygen concentration or the concentration of a reducing gas component with an arrangement of just two measuring electrodes by using the sensor according to the present invention for determining a concentration of gas components in gas mixtures having a first measuring electrode (mixed potential electrode) which has little or no catalytic effect on the establishment of an equilibrium in the gas mixture and a second measuring electrode (equilibrium electrode) which catalyzes the establishment of an equilibrium in the gas mixture as well as a solid electrolyte that is conductive for oxygen ions arranged between the two measuring electrodes, with the two measuring electrodes being exposed to the gas mixture. Due to the fact that at least the first measuring electrode is a cermet electrode, where at least one metal oxide component of the cermet electrode is capable of reversible incorporation of oxygen, the potential of this first measuring electrode is kept almost constant in the range around  $\lambda \approx 1$ . Thus, the first measuring electrode is the reference electrode in this operating state of the internal combustion engine, while the second measuring electrode functions as the working electrode. If the operating state of the internal combustion engine

changes to a range with  $\lambda > 1$ , then the potential of the second measuring electrode is almost constant, while the potential of the first measuring electrode is variable and is determined essentially by the concentration of the reducing gas components. Thus in this case the second measuring electrode is the reference electrode and the first measuring electrode is the working electrode.

Suitable metal oxide components for the first measuring electrode include, for example, the mixed oxides such as  $\text{TiNiNbO}_x$  or  $\text{FeNiMnO}_4$ . Furthermore, a noble metal such as gold may also be incorporated into the first measuring electrode. It is thus possible to adapt the potential of the first measuring electrode very accurately to the requirements of a given application.

In a preferred embodiment of the present invention, a reference electrode additionally exposed to a reference gas is provided for the two measuring electrodes exposed to the gas mixture. The measuring electrodes may be arranged side by side, i.e., both in the same layer of a multilayer sensor. However, it is also conceivable for the two measuring electrodes to be arranged one after the other in different layers, starting from an outer side of the sensor in the direction of the reference electrode. One layer between the two measuring electrodes must be sufficiently porous so that it allows a sufficiently rapid establishment of an equilibrium in the constantly changing concentrations of the individual exhaust gas components. One measuring electrode corresponds to the mixed potential electrode based on oxygen-storing metal oxide components and the other measuring electrode is designed as an equilibrium electrode.

It has proven advantageous to arrange the mixed potential electrode closer to the exhaust gas because it has an



especially stable and constant potential in rapid gas changes at lambda values around 1. In addition to an equilibrium electrode which naturally has a catalytic activity, it is also conceivable to incorporate additional catalysts or promoters into the porous intermediate layer, although of course not in the immediate vicinity of the mixed potential electrode. In this way, it is possible to have a controlled influence on the establishment of an equilibrium in the mixture, thus yielding the possibility of using other metal components that are not catalytically active for the equilibrium electrode.

With the help of this preferred arrangement with a total of only three electrodes, the oxygen concentration and the concentration of the reducing gas components can be determined simultaneously in certain operating states and thus the status of the lambda value can be determined directly. This permits a much more rapid and accurate establishment of the control status of the internal combustion engine. In addition, such a sensor can be implemented in an especially simple and inexpensive manner.

#### Brief Description Of The Drawings

Figure 1 shows a schematic sectional view through a sensor.

Figure 2 shows a schematic sectional view through another embodiment of a sensor.

#### Detailed Description

Figure 1 shows a sensor 10 which can be used for determination of the concentration of gas components in gas mixtures, in particular the exhaust gases of internal combustion engines. Such a sensor 10 is preferably composed of individual ceramic layers which may be structured in a known way by screen printing, lamination, cutting, sintering or the like. Sensor 10 contains an electrochemical measuring cell 12 having a

first measuring electrode 14 and a second measuring electrode 16, with a porous oxygen ion conducting layer 18 extending between two measuring electrodes 14, 16. A heating element 22 is arranged beneath second measuring electrode 16 in a layer 20 which at least conducts heat well. Heating element 22 includes a resistance element 24, designed as a meandering element here, and it functions to establish or control an operating temperature of sensor 10. Second measuring electrode 16 is composed of a noble metal cermet, e.g., based on a noble metal such as platinum. This second measuring electrode 16 is referred to below as equilibrium electrode 16 because of the catalytic activity of these noble metals with regard to the equilibrium reaction between oxygen and reducing gas components of the exhaust gas as explained below. As also to be explained below, first measuring electrode 14 has little or no catalytic activity in certain operating states of the internal combustion engine, which can be characterized by a lambda value, and it is referred to below as mixed potential electrode 14.

During combustion of a fuel/air mixture in the internal combustion engine, reducing gas components which can react with the oxygen and are thus in a thermodynamic equilibrium with it are formed in variable amounts. In addition to a temperature-dependent equilibrium status of this reaction, the kinetics of the reaction is especially important for establishing the equilibrium. It may essentially be assumed that the temperature of the exhaust gas drops with an increase in the distance of sensor 10 from the engine, and thus it becomes more difficult for a thermodynamic equilibrium to be established from a kinetic standpoint. Due to the noble metals such as platinum, palladium and rhodium used in equilibrium electrode 16, establishment of this equilibrium is catalyzed. Thus, the potential of equilibrium electrode 16 is determined essentially by the oxygen concentration.

The potential of mixed potential electrode 14, however, does not depend on the oxygen concentration, at least in some ranges, but instead it is a function of the concentration of reducing gas components. It is thus possible to influence the potential of mixed potential electrode 14 in a controlled manner by selecting at least one metal oxide component capable of reversible incorporation of oxygen. Such a mixed potential electrode 14 may be made mostly of  $\text{TiNiNbO}_x$  or  $\text{FeNiMnO}_4$ . It is also conceivable to use metal oxides such as  $\text{Mn}_2\text{O}_3$  and  $\text{CeO}_2$ . In addition, the cermet electrode may also contain as an added metal component a noble metal such as gold or silver. In this way, the potential of mixed potential electrode 14 can be adapted individually to the requirements of given applications.

In an operating mode of internal combustion engine where  $\lambda \approx 1$ , the oxygen concentration directly at a surface of mixed potential electrode 14 is kept almost constant due to the added metal oxide components. A capacity for incorporation and disincorporation of oxygen in a mixed potential electrode 14 determines a lambda range in which the potential of mixed potential electrode 14 is almost constant. However, the potential on equilibrium electrode 16 in such an operating mode of the internal combustion engine is exposed to great variations, because there are great variations in oxygen concentration precisely in such a lambda range. Thus at  $\lambda \approx 1$ , mixed potential electrode 14 can be used as a reference electrode, while equilibrium electrode 16 can be used as a working electrode 16. Then a detection voltage U which is a direct measure of the oxygen concentration of the gas mixture can be picked off via electrochemical measuring cell 12.

When the operating mode of the internal combustion engine changes to a range of  $\lambda > 1$ , then the potential of mixed potential electrode 14 changes greatly with a change in the

concentration of the reducing gas components. However, the potential of equilibrium electrode 16 is almost constant at high oxygen concentrations. Thus in this case, equilibrium electrode 16 functions as the reference electrode and mixed potential electrode 14 functions as the working electrode. Then a detection voltage U corresponding to the concentration of the reducing gas components can be picked off via electrochemical measuring cell 12.

In principle, an arrangement of two measuring electrodes 14, 16 may be in the opposite order from that shown here, but in the case of the arrangement shown here, additional promoters or catalysts that support the establishment of an equilibrium may be incorporated into layer 18. In this way it is possible to vary the composition of equilibrium electrode 16 to a great extent, and it is not necessary to use such relatively expensive noble metals as platinum or palladium.

Figure 2 shows a preferred additional embodiment of sensor 10. In addition to two measuring electrodes 14, 16 described above, sensor 10 has another reference electrode 26. Reference electrode 26 is above a reference channel 28 which is filled with a reference gas. Heating device 22 is used first for heating sensor 10 and also for heating the reference gas. Between reference electrode 26 and equilibrium electrode 16 there is a layer 30 composed of a solid electrolyte that is conductive for oxygen ions.

Such a sensor 10 has a first electrochemical measuring cell 32, which includes mixed potential electrode 14 and reference electrode 26, and a second electrochemical measuring cell 34, which includes equilibrium electrode 16 and reference electrode 26.

With the help of this very simple arrangement with only three

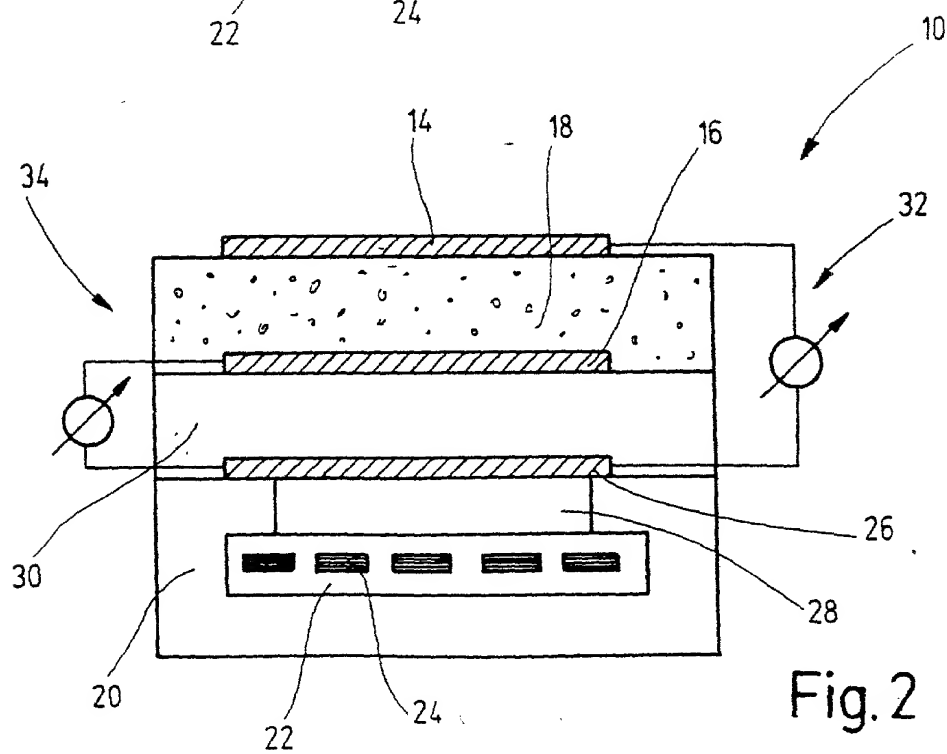
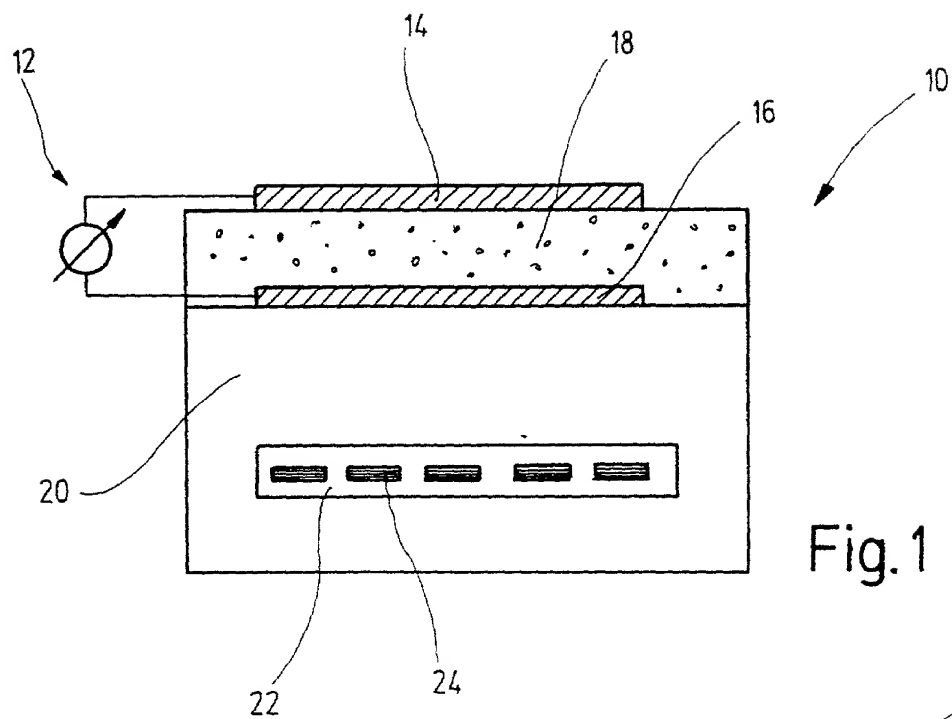
electrodes, the oxygen concentration and the concentration of the reducing gas components can be measured simultaneously as a function of the operating mode of the internal combustion engine. In this way, a lambda value can be determined very rapidly and with high precision.

Thus, for example, at a lambda value  $> 1$ , the potential of mixed potential electrode 14 depends essentially on the concentration of the reducing gas components, as mentioned above, and thus it can be picked off as a detection voltage  $U_1$  via electrochemical measuring cell 32. In the same operating mode, a potential difference between equilibrium electrode 16 and reference electrode 26 can also be detected if the reference gas has a sufficiently different oxygen concentration. The potential difference then leads to a detection voltage  $U_2$  which can be picked off at electrochemical measuring cell 34 and is a direct measure of the oxygen concentration.

In addition to the arrangement shown here, where measuring electrodes 14, 16 are arranged in successive layers of sensor 10, an arrangement in one and the same layer is also conceivable. In this way, sensor 10 is also simpler to manufacture, i.e., fewer steps are involved.

### Abstract Of The Disclosure

A sensor for determining a concentration of gas components in gas mixtures having a first measuring electrode (mixed potential electrode) which has little or no catalytic effect on the establishment of an equilibrium in the gas mixture and a second measuring electrode (equilibrium electrode) which catalyzes the establishment of an equilibrium in the gas mixture as well as a solid electrolyte that is conductive for oxygen ions arranged between the two measuring electrodes, with the two measuring electrodes being exposed to the gas mixture. At least the first measuring electrode (16) is a cermet electrode, where at least one metal oxide component of the cermet electrode is capable of reversible incorporation of oxygen.



**DECLARATION AND POWER OF ATTORNEY**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled **SENSOR FOR DETERMINING A CONCENTRATION OF GAS COMPONENTS IN GAS MIXTURES**, the specification of which was filed as International Application No. PCT/DE00/02124 on June 29, 2000.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application(s) for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

**PRIOR FOREIGN APPLICATION(S)**

Number	Country Filed	Day/Month/Year	Priority Claimed Under 35 USC 119
199 32 048.9	Fed. Rep. of Germany	July 9, 1999	Yes



2 And I hereby appoint Richard L. Mayer (Reg. No. 22,490) and Gerard A. Messina (Reg. No. 35,952) my attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Please address all communications regarding this application to:

KENYON & KENYON  
One Broadway  
New York, New York 10004

Please direct all telephone calls to Richard L. Mayer at (212) 425-7200.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful and false statements may jeopardize the validity of the application or any patent issued thereon.

100  
Inventor: Jens Stefan SCHNEIDER

Inventor's Signature: \_\_\_\_\_

Date: 3. Mar. 2001

Residence: 409 Quail Hollow  
Anderson, South Carolina 29621 SC  
United States of America

Citizenship: Federal Republic of Germany

Post Office Address: Same as above.

200 Inventor: Gerhard HOETZEL

Inventor's Signature: Gerhard Hoetzel

Date: 19th february 2001

Residence: Mahlestr. 62 A  
70376 Stuttgart  
Federal Republic of Germany DEX

Citizenship: Federal Republic of Germany

Post Office Address: Same as above.

300 Inventor: Bernd SCHUMANN

Inventor's Signature: Bernd Schumann

Date: 15<sup>th</sup> February 2001

Residence: Daimlerstr. 23  
71277 Rutesheim  
Federal Republic of Germany DEX

Citizenship: Federal Republic of Germany

Post Office Address: Same as above.

400  
Inventor: Thomas MOSER

Inventor's Signature: Thomas Moser

Date: 19<sup>th</sup> February 2001

Residence: Herrenwiesenweg 7  
71701 Schwieberdingen  
Federal Republic of Germany DE

Citizenship: Federal Republic of Germany

Post Office Address: Same as above.